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(54) GLASS REINFORCED THERMOPLASTIC COMPOSITIONS AND METHODS OF MAKING SAME

(71) We, LIQUID NITROGEN PROCESSING CORPORATION, of 412 King Street, Malvern, Pennsylvania 19355, United States of America, a Corporation organised and existing under the laws of the State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to glass reinforced thermoplastic compositions and methods for making the same. More particularly, the present invention is directed to thermoplastic composites reinforced with glass fibers and provided with metallocene coupling agents.

The use of composite thermoplastics, particularly those containing chopped glass fibers is expanding rapidly. More specifically, thermoplastic composites are penetrating engineering applications in which strength and high temperature properties are of great importance. Such applications include tool and machine housings, gears and connecting blocks, and many others.

A quite early development in the field of glass reinforced thermoplastics was the addition of a coupling agent to improve both mechanical properties and resistance to moisture. A coupling agent is a substance which can form a mechanical and/or chemical bond between the glass fibers and the thermoplastic resins. In the current state of the art, a physio-chemical linking agent is most commonly applied to the glass fibers as a sizing. Nearly all of such coupling or linking agents are silanes.

The silanes are ambifunctional compounds, containing groups which are easily hydrolyzed and replaced by siloxane linkages to the

glass fibers, and groups that have a specific reactivity toward the thermoplastic resin. As an example, gamma (γ)-Aminopropyltrimethoxysilane is often used in glass fiber reinforced thermoplastic composites wherein nylon 6 is the thermoplastic resin.

Although silane coupling agents function exceedingly well in many applications, several deficiencies are apparent. Thus, in many systems the composite produced does not result in optimum theoretical reinforcement. Moreover, in high temperature resin systems the silanes degrade in processing, and a coupled composite system is not achieved. Particularly difficult coupling problems are encountered with reinforced polypropylene composites.

According to one aspect of the invention there is provided a reinforced thermoplastic composition comprising from 40 to 95 weight per cent of a thermoplastic resin, from 5 to 60 weight per cent of glass fibers, and from 0.05 to 5.5 weight per cent of a coupling agent, said coupling agent comprising at least one metallocene selected from titanocene dihalides, zirconocene dihalides, hafnocene dihalides, titanocene disulfonates, stable derivatives of the foregoing, and combinations of a stable ferrocene derivative with a silane, said silane being reactive with said stable ferrocene derivative and being selected from alkoxysilanes and acryloxysilanes.

According to another aspect of the invention there is provided a method for making reinforced thermoplastic composites comprising the steps of blending 5 to 60 weight per cent of glass fibers with 40 to 95 weight per cent of a thermoplastic resin, and incorporating 0.05 to 5.5 weight per cent of a metallocene coupling agent in said composite, said metallocene being selected from titanocene dihalides, zirconocene dihalides, hafno-

cene dihalides, titanocene disulfonates, stable derivatives of the foregoing, and combinations of a stable ferrocene derivative and a silane, said silane being reactive with said stable ferrocene derivative and being selected from the group consisting of alkoxysilanes and acryloxysilanes.

The metallocene coupling agent may be applied directly to the glass fibers prior to blending with the thermoplastic resin, or the metallocene may be mixed with the thermoplastic resin prior to or during the blending with the glass fibers.

Virtually any thermoplastic resin which may be conventionally reinforced with glass fibers may be used in the reinforced thermoplastic compositions of the present invention. Such thermoplastic resins include polystyrene, polypropylene, polyvinyl chloride, thermoplastic urethanes, polyimides, and the nylons including nylon 6/10, nylon 6/6, nylon 6, nylon 6/12, nylon 6/9, nylon 11, and nylon 12. Other thermoplastic resins conventionally used in reinforced composites for various molding operations will be readily apparent to those of ordinary skill in the art.

Traditional glass reinforced thermoplastic compositions generally contain 40 to 95 weight per cent of a thermoplastic resin and 5 to 60 weight per cent of glass fibers, although these ranges may be broadened for special applications. In addition, conventional reinforced thermoplastic composites include small amounts of coupling agents and may include various percentages of additional inert components such as pigments and fillers.

It will be understood by those of ordinary skill in the art that in order to be suitable for formation of glass reinforced composites, the glass must be fibrous. Although fibrous glass is provided in many forms, including glass fiber mats and spun roving, continuous glass roving and chopped glass strands are generally preferred.

At present, virtually all commercially available glass fiber is sold with one or more sizing ingredients already applied. Such sizing ingredients may include a lubricating agent to prevent chafing of glass fibers by mechanical contact and a cementitious material such as polyvinyl alcohol as a film former. In addition, glass fibers to be incorporated in the reinforced thermoplastic composites of the present invention may be treated with traditional coupling agents, typically silanes, as discussed more fully below.

The improved coupling agents of the present invention are selected from the general class known as metallocenes. Metallocenes are cyclopentadienyl derivatives or complexes of transition metals or transition metal halides. Particularly important metallocenes selected for the present invention are those which are dicyclopentadienyl complexes [e.g., $(C_5H_5)_2M$ or $(C_5H_5)_2MX_{1-3}$, where M is a transition

metal and X is a halogen] wherein the transition metal or transition metal halide is sandwiched between the two aromatic cyclopentadienyl rings and is bonded by a coordinated bond, usually referred to as a pi bond.

The metallocenes are capable of forming a chemical and/or mechanical link to thermoplastic resins. In addition, many metallocenes are capable of bonding directly to glass fibers, and others are capable of bonding indirectly to glass fibers through a silane coupling agent.

The metallocene compounds which are capable of linking directly to glass, and which do not need silane coupling agents, include titanocene dihalides, zirconocene dihalides, hafnocene dihalides, and titanocene disulfonates. While titanocene, zirconocene or hafnocene dichlorides are particularly preferred, diiodides, dibromides and difluorides will behave analogously and may be used in a similar manner. In addition, stable ring substituted derivatives of the titanocenes, zirconocenes and hafnocenes may also be employed. Other metallocenes are capable of linking to a thermoplastic resin, but do not have a great affinity for glass. Such metallocenes, which include the ferrocene derivatives, must be used in combination with other coupling agents, such as the traditional silane coupling agents, in order to produce an indirect link to the glass fibers. Examples of suitable ferrocene derivative coupling agents include ferrocenoyl dichloride; ferrocene 1,1' dicarboxylic acid; ferrocene 1,1' diamine; 1,1' di(chloromercuri) ferrocene; 1,1' dihydroxymethyl ferrocene and N,N' dimethylaminomethyl ferrocene. Other suitable ferrocene derivatives may be determined by those of ordinary skill in the art.

In order to provide the desired indirect link between the ferrocene derivative and the glass fibers, it is necessary to choose an intermediate coupling agent which is capable of reacting with the ferrocene derivative. Suitable silane coupling agents for this purpose are alkoxysilanes and acryloxysilanes. Examples of suitable alkoxysilanes include, but are not limited to trialkoxysilylureas, aminoalkyltrialkoxysilanes, chloroalkyltrialkoxysilanes, glycidoxyalkyltrialkoxysilanes, and isocyanatoalkyltrialkoxysilanes. The optimum combinations of ferrocene derivatives and silane coupling agents can be chosen by those of ordinary skill in the art by prudent consideration of the chemical reactivities of the various ferrocene derivatives and silanes.

Although the non-ferrocene metallocenes previously listed do not require the use of a silane coupling agent, silanes may be advantageously employed with the non-ferrocene metallocenes in order to further enhance the properties of the reinforced thermoplastic compositions of the present invention. Thus, the typical alkoxysilanes and acryloxysilanes listed above for use with the ferrocene

derivatives may also be employed with titanocenes, zirconocenes and hafnocenes.

Although the mechanism of interaction is not completely certain in every case, and applicants do not wish to be bound by any particular theory, it is thought that the ferrocene derivatives interact with the organic or carbon portion of the silanes, whereas the zirconocenes, titanocenes and hafnocenes are thought to interact with the silanol groups of the silanes. Thus, in the titanocenes, zirconocenes and hafnocenes, the halide bonds to the transition metal may be displaced with silanol bonds, splitting out the alkoxy moieties. The purpose of this reaction is to allow more sites for reaction with glass fibers through the unreacted silanol bonds of the silane. Where no silane coupling agent is used, the halides are displaced to form direct siloxane linkages to the glass.

The amount of metallocene incorporated into a reinforced thermoplastic composite may vary widely, and will depend to a certain extent upon the manner of incorporation. If the metallocene is applied directly to the glass fibers, the total amount of metallocene present is preferably between 0.05 and 1.0 weight per cent of the total composite. If, on the other hand, the metallocene is added to the thermoplastic resin, or the composite premix, the total amount of metallocene present is preferably between 0.2 and 3.0 weight per cent.

The amount of silane coupling agent used in connection with a metallocene may also vary widely, and in the case of titanocenes, zirconocenes and hafnocenes may be completely omitted. For optimum cost and performance with any of the metallocenes, the silane coupling agent is preferably present in an amount of 0.05 to 2.5 weight per cent of the total composite. Thus, the total amount of coupling agent, including both silane and metallocene, may be up to 5.5 weight per cent.

The metallocene coupling agent with or without a traditional silane coupling agent may be incorporated into the composite at various stages. For example, where it is desired to apply the coupling agent directly

to the glass fibers, the coupling agent may be applied along with the standard sizing ingredients to glass roving before chopping. Alternatively, the coupling agent may be dissolved in a suitable solvent such as benzene and then added to the chopped glass fibers which are subsequently tumbled.

If desired, it is also suitable to mix the coupling agent directly into the thermoplastic resin before blending with the glass fibers, or into the thermoplastic resin/chopped glass premix prior to extrusion. Generally speaking, it is easier for a compounder to add the coupling agent to the premix prior to compounding. However, it is more efficient and effective to coat the fiberglass directly with the coupling agent, as is indicated above with the greater amounts of coupling agent being required when incorporating into the resin or resin-glass fiber premix.

The invention will now be illustrated in more detail with reference to the following specific, non-limiting examples. The physical properties of articles molded with the glass fiber reinforced thermoplastic compositions of the following examples were determined by the following ASTM standard tests for glass reinforced thermoplastics:

Property	ASTM Test
Tensile strength and elongation	D638
Flexural strength and modulus	D790
Impact strength (notched and unnotched)	D256
Heat distortion	D1822
Mold shrinkage	D955

EXAMPLE I

Two premixes (i.e., tumbled blends of components employed directly in injection molding) were prepared one without a metallocene coupling agent and one with a metallocene. Each of the premixes was molded into ASTM shots. Both composites were prepared with polypropylene supplied by Avisun Corporation and Owens Corning Fiberglas designated P-59B (incorporated as sized chopped 1/4" fibers). The following properties were observed for the two composites:

	Component	Parts by Weight	
		A	B
100	Polypropylene	70	70
	Fiberglas P-59B	30	30
	Titanocene Dichloride	0	0.75
	Properties	A	B
105	Tensile strength psi	8,100	11,560
	Elongation %	2.8	3.1
	Izod impact, notched (1/4" bar)	1.6	3.9
	Izod impact, unnotched (1/4" bar)	6.2	9.8

From the above it is evident that titanocene dichloride effects an enhancement in the properties of polypropylene/glass fiber composites.

5 EXAMPLE II

As a further control ASTM shots were prepared as in Example I with neat polypropylene (i.e., polypropylene without any glass fibers). It was found that the addition of titanocene dichloride as in sample B of Example I did not substantially affect the physical properties of the resin. The tensile strength of both neat polypropylene resin samples was 4,600 psi under the same testing conditions as in Example I.

EXAMPLE III

A premix molding was prepared under the same conditions as in Example I except that gamma (γ) - glycidoxypropyltrimethoxysilane manufactured by Dow Corning under the designation Z 6040 was also added. The composition and ASTM properties are as follows:

	Components	parts by weight
25	Polypropylene	70
	Glass fiber	30

55	Components
	Polypropylene
	Fiberglass
	Titanocene Dichloride
	Z 6040

60	Properties
	Mold shrinkage—1/8" in/in
	Tensile strength, psi
	Elongation %
	Flexural strength, psi
65	Flexural modulus, psi
	Izod impact, notched ft. lbs./in. (1/4" bar)
	Izod impact, unnotched ft. lbs./in. (1/4" bar)
	Heat distortion, 264 spi, °F

Titanocene dichloride	0.5	
Z 6040	0.5	30

Properties		
Tensile strength, psi	12,325	
Elongation %	3.25	
Izod impact, notched ft. lbs/in (1/4" bar)	5.1	35
Izod impact, unnotched ft. lbs/in (1/4" bar)	8.7	

It will be observed that a greater degree of enhancement is observed when incorporating a silane with the metallocene coupling agent. In addition, it may be noted that while some property improvement is obtained by addition of Z 6040 alone, the improvement is not substantial when compared with the use of titanocene dichloride alone as in sample B of Example I.

EXAMPLE IV

Extrusions (i.e. extruded blends of components in pellet form employed in injection molding) were prepared using a tumbled mix of the ingredients designated in Example III. No vacuum venting was employed in the extrusion. The amounts of each ingredient and the ASTM properties are listed below:

55	Components	Parts by Weight	
	Polypropylene	A	B
	Fiberglass	80	80
	Titanocene Dichloride	20	20
	Z 6040	0.5	0
60	Properties	0.5	0
	Mold shrinkage—1/8" in/in	A	B
	Tensile strength, psi	0.001	0.004
	Elongation %	10,940	7,000
	Flexural strength, psi	3.2	2—3
65	Flexural modulus, psi	13,500	8,600
	Izod impact, notched ft. lbs./in. (1/4" bar)	580,000	525,000
	Izod impact, unnotched ft. lbs./in. (1/4" bar)	2.0	1.2
		6.0	5—6
	Heat distortion, 264 spi, °F	300	285

70 EXAMPLE V

A premix molding using zirconocene dichloride was prepared and tested. The resulting composite was off-white, in contrast with the red-brown composite produced with titanocene dichloride. The composition and properties are listed below:

75	Components	parts by Weight
	Polypropylene	80
80	Glass fiber	20
	Zirconocene dichloride	0.5
	Z 6040	0.5
	Properties	
	Tensile strength, psi	11,200

Elongation %	4.1	85
Izod impact, notched, ft. lb./in (1/4" bar)	3.7	
Izod impact, unnotched ft. lbs./in (1/4" bar)	6.9	

EXAMPLE VI

A methanol solution containing 5% titanocene dichloride and 5% gamma (γ)-glycidoxypropyltrimethoxysilane was sprayed onto glass fiber roving designated P 673 by Owens Corning Fiberglas. The roving was subsequently dried and chopped into 1/4" lengths. After drying the total solids pickup was approximately 0.8%. A 30% glass fiber, 70%

polypropylene premix composite was then prepared, and the following physical properties were observed:

Properties		
5	Tensile strength, psi	11,900
	Elongation %	3.8
	Izod impact notched, ft. lbs./in. (1/4" bar)	2.9
10	Izod impact unnotched, ft. lbs./in. (1/4" bar)	8.0

EXAMPLE VII

Two premix formulations were prepared containing 20 parts by weight 1/4" chopped glass fibers designated 308A by Johns Mannville, and 80 parts by weight of polyvinylchloride made by Airco Chemical Company. Sample A was provided with 0.5 parts by weight diaminoferrocene and 0.5 parts by weight chloropropyltriethoxysilane, while sample B had no coupling agent. The properties of the two samples were as follows:

Properties			A	B
25	Tensile strength, psi		12,900	9,450
	Elongation %		2.4	2.9
	Flexural strength, psi		16,860	13,520
	Flexural modulus, psi		842,000	795,000
	Izod impact, notched, ft. lbs./in. (1/4" bar)		1.5	1.0
	Izod impact, unnotched, ft. lb./in. (1/4" bar)		6.8	5.0

EXAMPLE VIII

Two premix formulations were prepared containing thirty parts by weight of one quarter-inch chopped glass fibers designated 704.00 by Johns Mannville, and 70 parts by weight nylon 6 made by Monsanto Company. Sample A was provided with 0.5 parts

by weight ferrocene dicarboxylic acid and 0.3 parts by weight of a polyamine functional silane designated Z 6050 and made by Dow Corning. Sample B did not contain any coupling agents. The properties of the two composites are as follows:

Properties			A	B
45	Tensile strength, psi		25,400	20,230
	Elongation %		3.9	3.4
	Izod Impact, notched ft. lb./in. 1/4" bar)		2.5	1.8
	Izod Impact, unnotched ft. lb./in. (1/4" bar)		19.6	12.9

EXAMPLE IX

Two premix formulations were prepared containing twenty parts by weight of one-quarter inch chopped glass fibers made by Pittsburgh Plate Glass Company, and 80 parts by weight polystyrene made by Foster

Grant Company, Inc. Sample A was provided with 0.75 parts by weight titanocene dichloride and Sample B did not contain any coupling agent. The properties of the two composites are listed below:

Properties			A	B
60	Tensile strength, psi		12,540	11,350
	Elongation %		2.0	2.0
	Izod impact, notched ft. lb./in. (1/4" bar)		2.7	1.8
	Izod impact, unnotched ft. lb./in. (1/4" bar)		3.8	2.9

WHAT WE CLAIM IS:—

1. A reinforced thermoplastic composition comprising from 40 to 95 weight per cent of a thermoplastic resin, from 5 to 60 weight per cent of glass fibers, and from 0.05 to 5.5 weight per cent of a coupling agent, said coupling agent comprising at least one metallocene selected from titanocene dihalides, zirconocene dihalides, hafnocene dihalides, titanocene disulfonates, stable derivatives of the foregoing, and combinations of a stable ferrocene derivative with a silane, said silane being reactive with said stable ferrocene

derivative and being selected from alkoxy-silanes and acryloxysilanes.

2. A reinforced thermoplastic composition according to Claim 1 wherein said metallocene is selected from titanocene dihalides, hafnocene dihalides, zirconocene dihalides, titanocene disulfonates, and stable derivatives thereof.

3. A reinforced thermoplastic composition according to Claim 2 wherein said coupling agent is present in an amount of 0.05 to 1 weight per cent and is in the form of a coating on the glass fibers.

4. A reinforced thermoplastic composition according to Claim 2 wherein said coupling agent is present in an amount of 0.2 to 3 weight percent and is dispersed throughout the thermoplastic composition. 45
5. A reinforced thermoplastic composition according to Claim 2 wherein said coupling agent also includes from 0.05 to 2.5 weight per cent of a silane selected from alkoxy-silanes and acryloxysilanes. 50
- 10 6. A reinforced thermoplastic composition according to Claim 5 wherein said silane is selected from trialkoxysilylureas, aminoalkyl-trialkoxysilanes, glycidoxalkyltrialkoxysilanes, acryloxysilanes, and isocyanalkyltrialkoxysilanes. 55
- 15 7. A reinforced thermoplastic composition according to Claim 5 wherein said thermoplastic resin is polypropylene and said metallocene is titanocene dichloride. 60
- 20 8. A reinforced thermoplastic composition according to Claim 1 wherein said glass fibers are selected from continuous glass roving and chopped glass strand. 65
- 25 9. A reinforced thermoplastic composition according to Claim 1 wherein said thermoplastic resin is selected from polypropylene, polystyrene, polyvinyl chloride, polyurethane, polyimides and nylon. 70
- 30 10. A reinforced thermoplastic composition according to Claim 1 wherein said thermoplastic resin is polypropylene and said metallocene is titanocene dichloride. 75
- 35 11. A reinforced thermoplastic composition according to Claim 1 wherein said metallocene is a combination of a stable ferrocene derivative and a silane, and said silane is present in an amount of 0.05 to 2.5 weight per cent and is selected from trialkoxysilylureas, aminoalkyltrialkoxysilanes, glycidoxalkyltrialkoxysilanes, acryloxysilanes, and isocyanalkyltrialkoxysilanes. 80
- 40 12. A reinforced thermoplastic composition according to Claim 11 wherein said ferrocene derivative is selected from ferrocenoyl dichloride; ferrocene 1,1' dicarboxylic acid; ferrocene 1,1' diamine; 1,1' di(chloromercuri) ferrocene; 1,1' dihydroxymethyl ferrocene and N,N' dimethylaminomethyl ferrocene. 85
13. A method for making reinforced thermoplastic composites comprising the steps of blending 5 to 60 weight per cent of glass fibers with 40 to 95 weight per cent of a thermoplastic resin, and incorporating 0.05 to 5.5 weight per cent of a metallocene coupling agent in said composite, said metallocene being selected from titanocene dihalides, zirconocene dihalides, hafnocene dihalides, titanocene disulfonates, stable derivatives of the foregoing, and combinations of a stable ferrocene derivative and a silane, said silane being reactive with said stable ferrocene derivative and being selected from the group consisting of alkoxy-silanes and acryloxy-silanes. 90
14. A method for making reinforced thermoplastic composites according to Claim 13 wherein said coupling agent is applied to said glass fibers prior to blending said glass fibers with said thermoplastic resin. 95
15. A method for making reinforced thermoplastic composites according to Claim 13 wherein said coupling agent is added to the composite while blending said glass fibers with said thermoplastic resin. 100
16. A method for making reinforced thermoplastic composites according to Claim 13 wherein said coupling agent is added to said thermoplastic resin prior to blending said glass fibers with said thermoplastic resin. 105

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